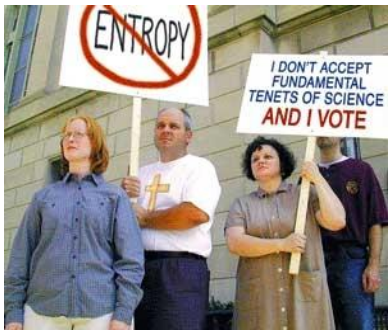
Chemical Thermodynamics

Reading: Ch 17, sections 1 – 9	Homework: Chapter 17: 27, 31, 37*, 39*, 41*, 43, 47, 49, 51*, 55, 57*, 59, 63, 71

* = 'important' homework question

The Second Law of Thermodynamics - ENTROPY



"We don't like the idea of an increasingly disordered universe"

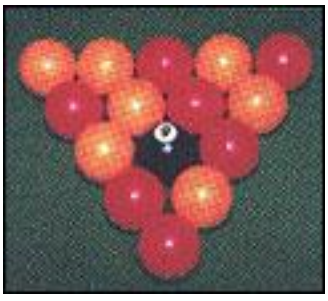
Key Idea and Definitions

The ENTROPY (note spelling), *S*, of the Universe increases (ΔS = +ve) for a *spontaneous* process.

Discussion: What is a spontaneous process? 'Being spontaneous' is a somewhat accurate analogy…

Entropy (S): A measure of the amount of disorder in a system, Symbol ***S***.

Discussion: What is *disorder*? Example, which has a higher degree of disorder (entropy) - a rack of pool balls before or after a break off??



Before

After

Entropy:

Entropy:

$\Rightarrow \Delta S = S_{(final)} - S_{(initial)} =$

Examples: Based on Entropy arguments alone, would you expect the following processes to be spontaneous (i.e. experience an increase in entropy upon completion)? Briefly explain.

1. H_2CO_3 (aq) $\rightarrow$ H_2O (l) + CO_2 (g)

Observation

"The 2nd law will take care of it"…

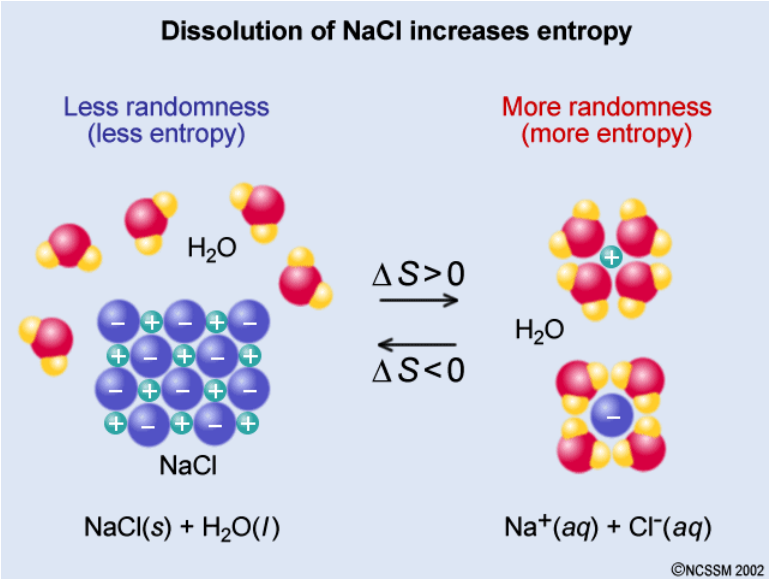
2. The air drying of washing up or clothes on a washing line

$$H_2O\ (l) \rightarrow H_2O\ (g)$$

Observation

3. NaCl (s) $\rightarrow$ NaCl (aq)

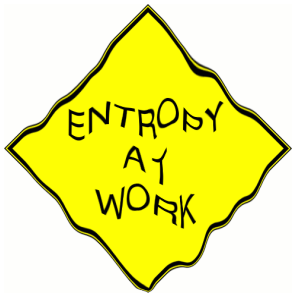
Observation (see more detailed figure below)



4. The diffusion of any gas

Observation

Task: List at least three entropy driven processes (see appendix for examples)



Just like with Enthalpy (H), each material has an inherent amount of entropy. All ***S*** values are measured in J/mol K and are always positive. **The magnitude of S indicates the relative amount of disorder for the material**.

Standard Entropy values can be used (in a similar way to ΔH_f values) to find ΔS for any reaction. See Appendix.

Example: Calculate ΔS for the following reaction:

$$CCl_4\,(l) \rightarrow CCl_4\,(g)\ ;\ \Delta S = \_\_\_\_\_$$

Given: CCl_4 (g), S = 309.4 J/molK
CCl_4 (l), S = 214.4 J/molK

What conclusion can you make regarding the evaporation of CCl_4 (l)?

Math considerations – the second law of thermodynamics

Entropy is temperature dependant – the hotter a material is the more entropy it has (standard entropies form Appendix C are calculated at $25^{o}C$, 1.00 atm). This fact is conveyed in the formal mathematical description of the 2nd law:

$$\mathbf{S = \frac{q_{rev}}{T}}$$

For chemical systems that do not do 'PV' work, $\Delta H = q$ (first law), therefore:

$$\mathbf{S = \frac{\Delta H}{T}}$$

Wrap up Discussion: If all spontaneous processes result in an increase in entropy, how can processes that result in a decrease in entropy (such as the freezing of water) for a material ever occur??

Gibbs Free Energy

Gibbs free energy (ΔG) for a reaction relates ΔH and ΔS for that reaction.

Simply, the mathematical sign of ΔG, determined via the Gibbs equation, determines if a reaction will ever work (is spontaneous); will never work (in non-spontaneous) or at equilibrium.

Spontaneous: ΔG < 0 Non-spontaneous: ΔG > 0 Equilibrium: ΔG = 0

Gibbs Free Energy Equation:

$$\Delta G = \Delta H - T\,\Delta S$$

The sign of ΔG (and, therefore, if a reaction is spontaneous) depends on the signs of ΔH and ΔS. See appendix.

Task: Complete the following table / determine the sign of ΔG

ΔH	ΔS	ΔG	spontaneous
-ve	-ve		
-ve	+ve		
+ve	-ve		
+ve	+ve		

As with ΔH and ΔS, ΔG is a state function.

ΔG values follow the same 'state function' math rules as the ΔH and ΔS, so can be determined from these quantities. Slides

'Huge' worked Example: The thermite reaction is used to weld railway tracks:

$$Fe_2O_3\,(s) + 2\,Al\,(s) \rightarrow 2\,Fe\,(s) + Al_2O_3\,(s)$$

Based on the below data, determine if this reaction is spontaneous at 25°C and quote the value of ΔG in kJ/mol

Given:

$\Delta H_f\ Fe_2O_3\ (s) = -822.16$ kJ/mol
$\Delta H_f\ Al_2O_3\ (s) = -1669.9$ kJ/mol

S Fe_2O_3 (s) = +89.96 J/molK
S Al_2O_3 (s) =+51.00 J/molK
S Fe (s) = +27.15 J/molK
S Al (s) = +25.32 J/molK

Plan: Find ΔH, ΔS, and then find ΔG

Free Energy and Equilibrium

Recall: For and equilibrium, $\Delta G = 0$. In terms of the equilibrium constant K and other variables

$$\Delta G = -RT \ln K$$

Where: K = equilibrium constant (no units)
ΔG = Gibbs Free energy (kJ/mol)
R = 8.314 J/molK
T = temperature in Kelvin

Task: Rearrange the above equation to find an expression for K in terms of ΔG

Group activity: Use the standard ΔG values in appendicies to find K at $25^{o}C$ for:

$$N_2\,(g) + 3\,H_2\,(g) \rightarrow 2\,NH_3\,(g)$$

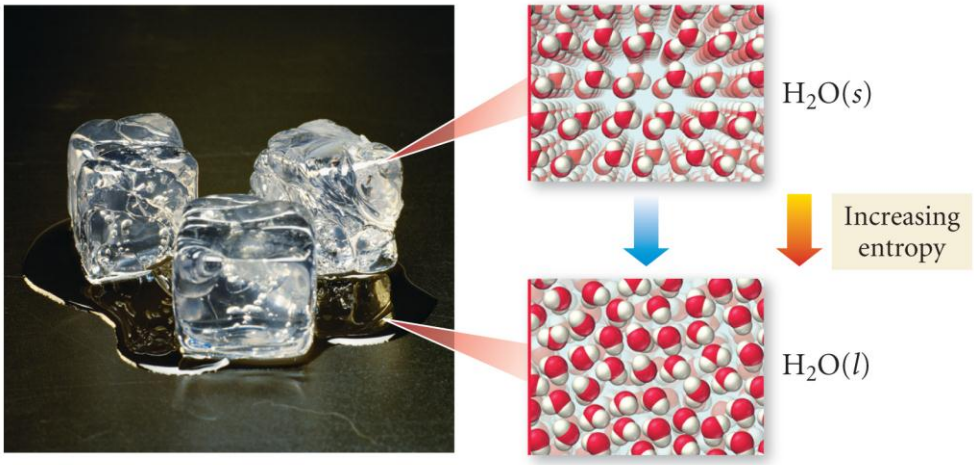
Plan: Find ΔG, find K

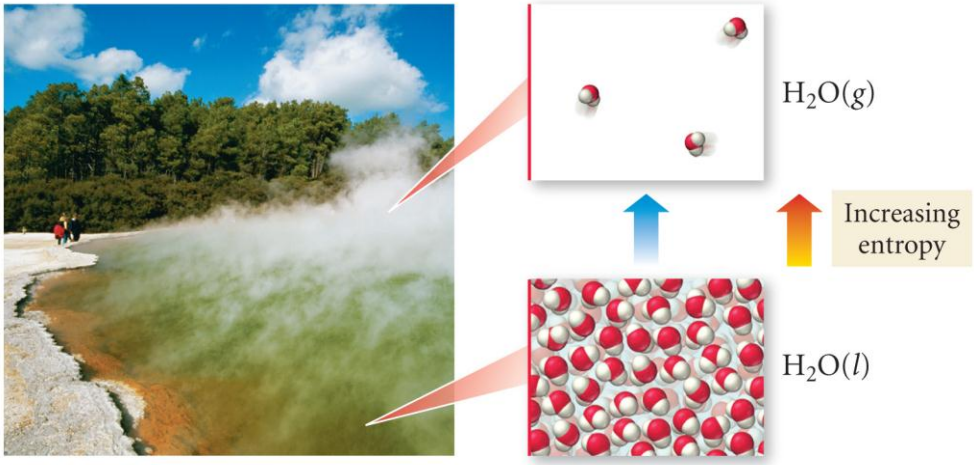
"Gibbs"

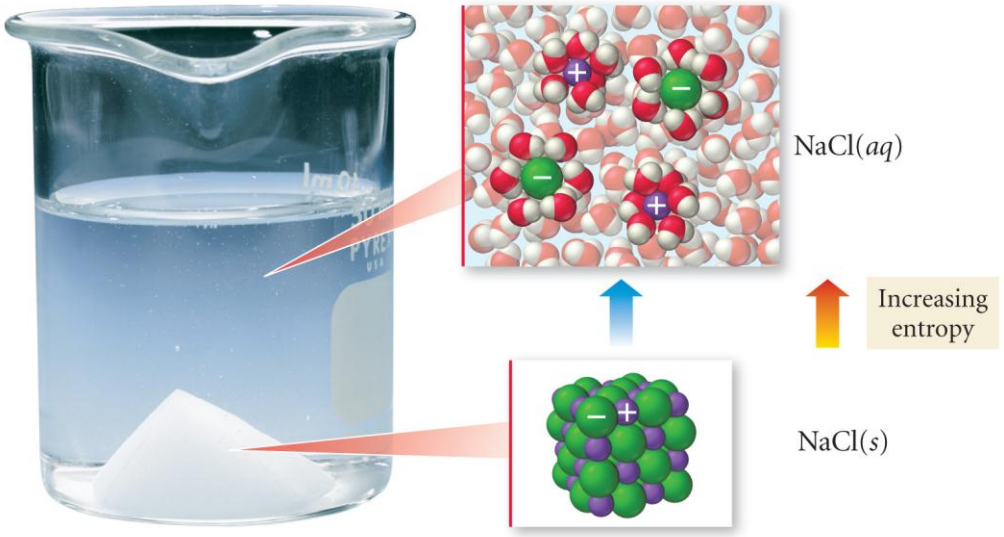
Question 1 (25 points): Using the thermodynamic information given in the data sheet, calculate ΔG^o for the following reaction:

$$Fe_2O_{3\,(s)} + 6\,HCl_{\,(g)} \rightarrow 2\,FeCl_{3\,(s)} + 3\,H_2O_{\,(g)}$$

Appendix







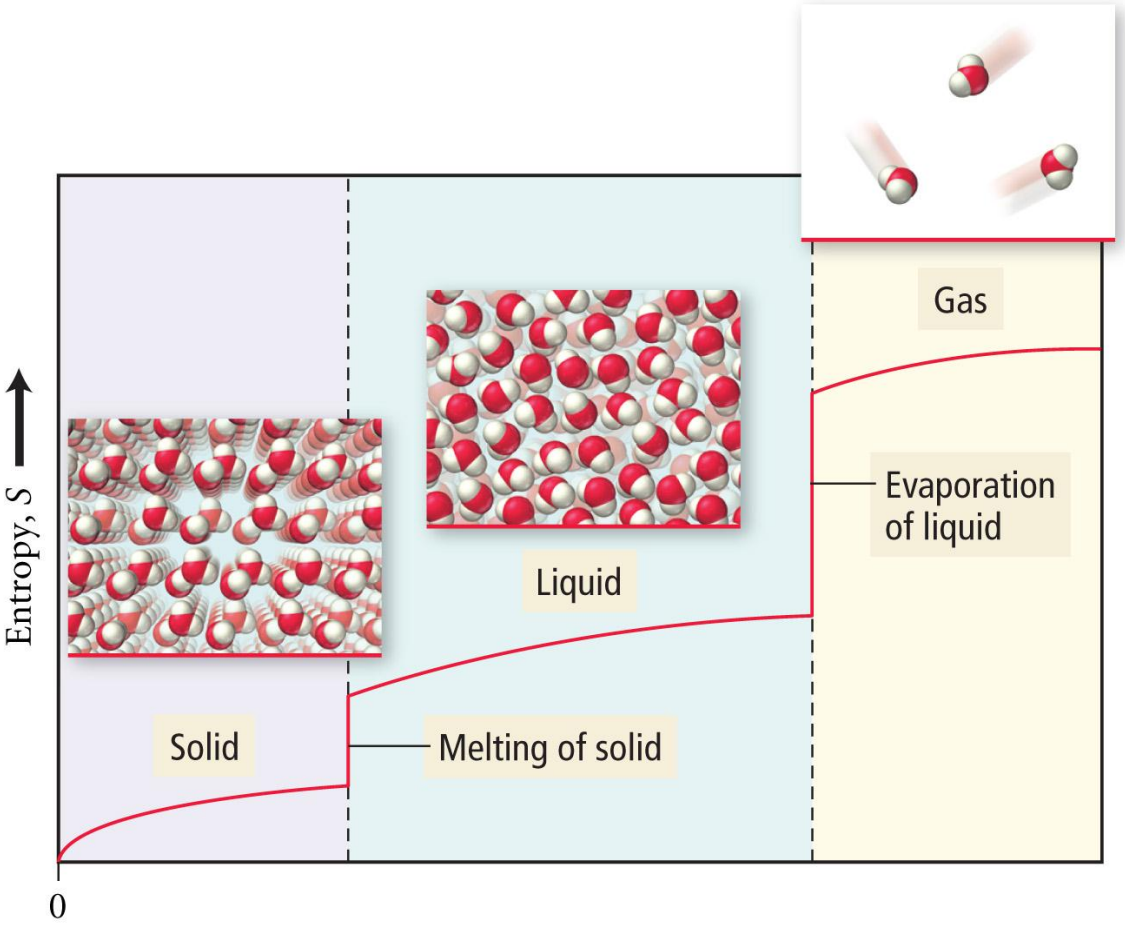
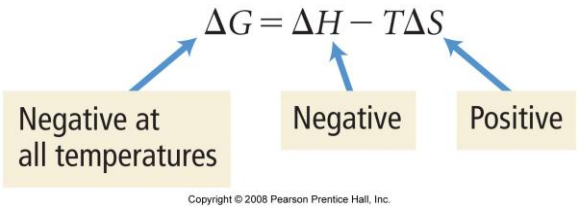


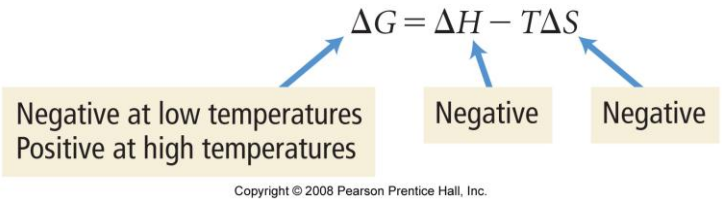
TABLE 17.2 Standard Molar Entropy Values ($S°$) for Selected Substances at 298 K

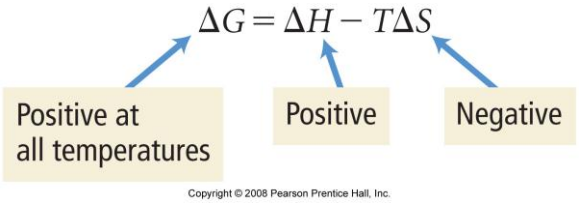
Substance	$S°$ (J/mol · K)	Substance	$S°$ (J/mol · K)	Substance	$S°$ (J/mol · K)
Gases		**Liquids**		**Solids**	
$H_2(g)$	130.7	$H_2O(l)$	70.0	$MgO(s)$	27.0
$Ar(g)$	154.8	$CH_3OH(l)$	126.8	$Fe(s)$	27.3
$CH_4(g)$	186.3	$Br_2(l)$	152.2	$Li(s)$	29.1
$H_2O(g)$	188.8	$C_6H_6(l)$	173.4	$Cu(s)$	41.6
$N_2(g)$	191.6			$Na(s)$	51.3
$NH_3(g)$	192.8			$K(s)$	64.7
$F_2(g)$	202.8			$NaCl(s)$	72.1
$O_2(g)$	205.2			$CaCO_3(s)$	91.7
$Cl_2(g)$	223.1			$FeCl_3(s)$	142.3
$C_2H_4(g)$	219.3				

TABLE 17.1 The Effect of ΔH, ΔS, and T on Spontaneity

ΔH	ΔS	Low Temperature	High Temperature	Example
−	+	Spontaneous ($\Delta G < 0$)	Spontaneous ($\Delta G < 0$)	$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$
+	−	Nonspontaneous ($\Delta G > 0$)	Nonspontaneous ($\Delta G > 0$)	$3\,O_2(g) \longrightarrow 2\,O_3(g)$
−	−	Spontaneous ($\Delta G < 0$)	Nonspontaneous ($\Delta G > 0$)	$H_2O(l) \longrightarrow H_2O(s)$
+	+	Nonspontaneous ($\Delta G > 0$)	Spontaneous ($\Delta G < 0$)	$H_2O(l) \longrightarrow H_2O(g)$







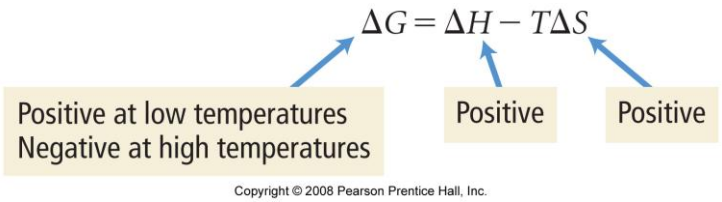
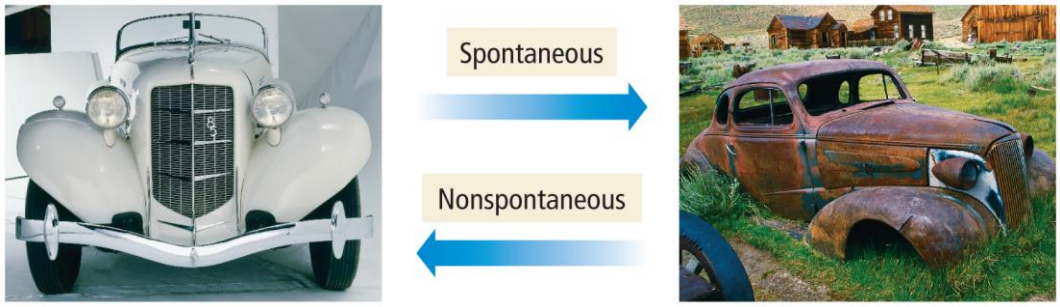
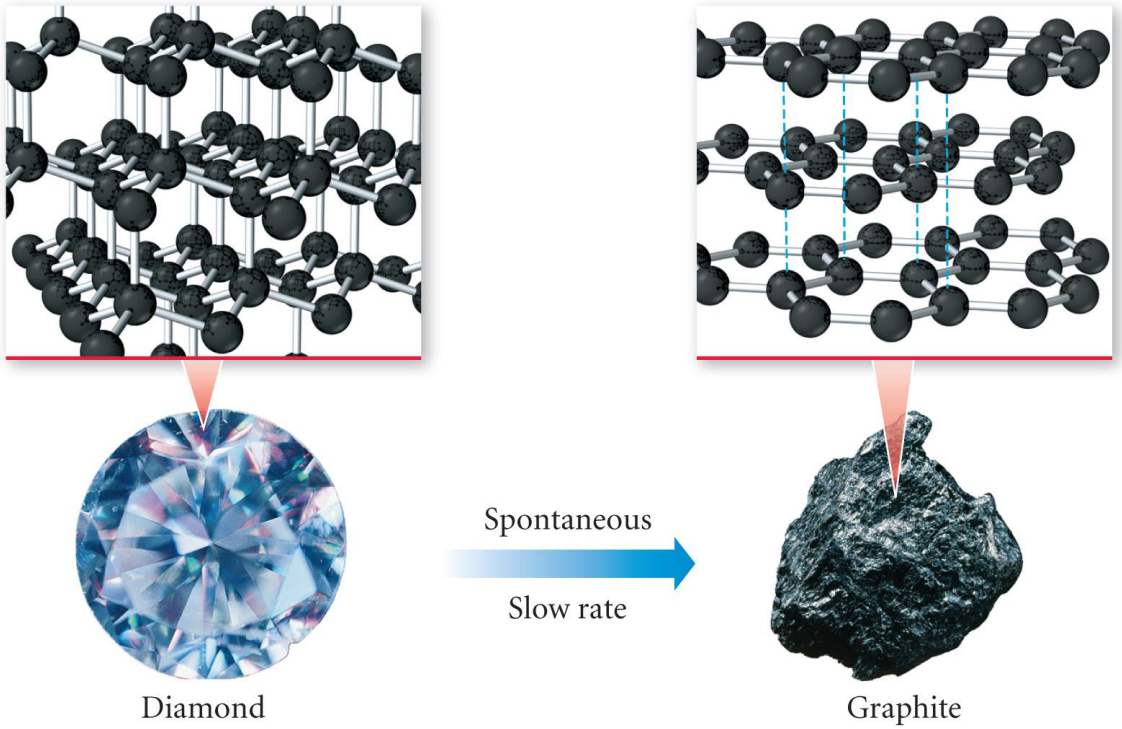


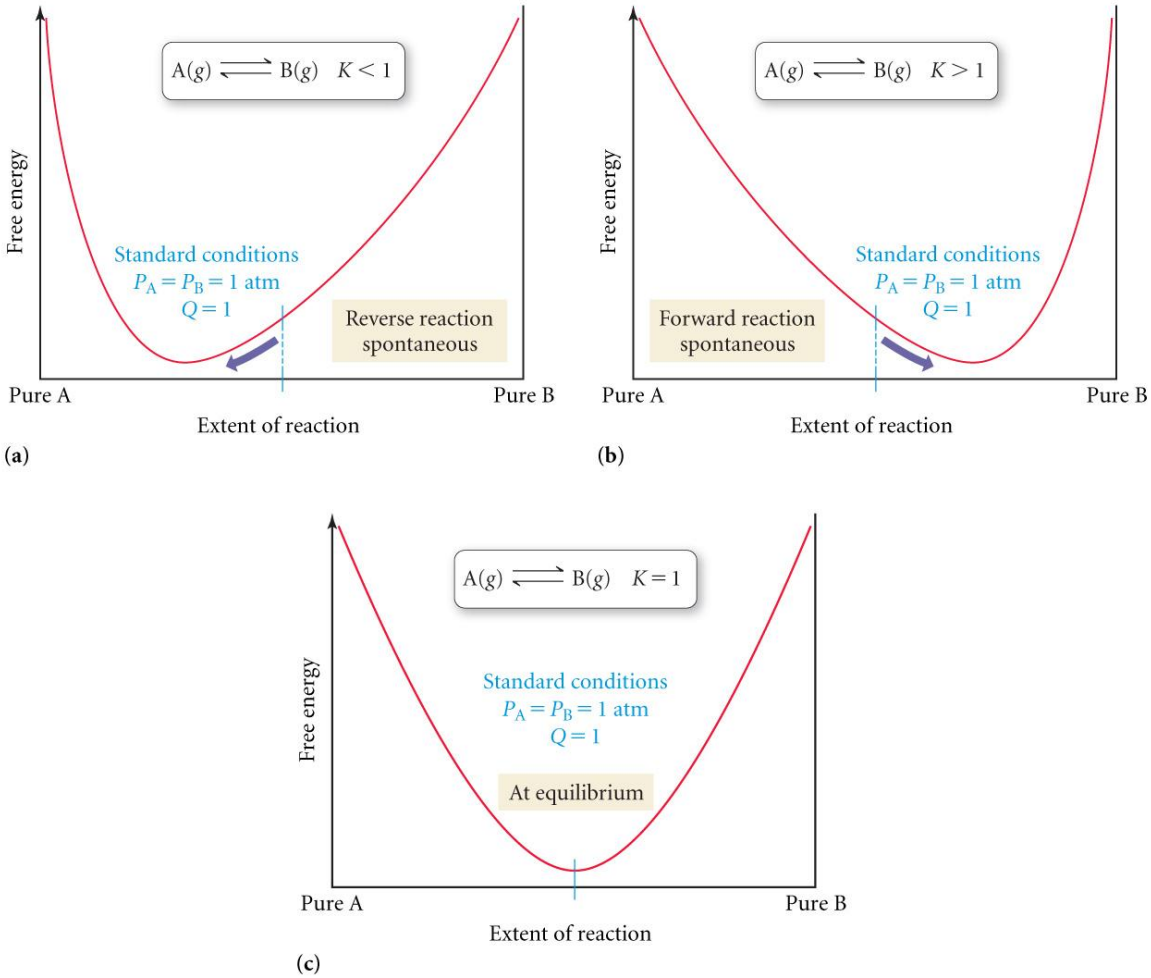
TABLE 17.3 Standard Molar Free Energies of Formation (ΔG_f°) for Selected Substances at 298 K

Substance	ΔG_f° (kJ/mol)	Substance	ΔG_f° (kJ/mol)
$H_2(g)$	0	$CH_4(g)$	−50.5
$O_2(g)$	0	$H_2O(g)$	−228.6
$N_2(g)$	0	$H_2O(l)$	−237.1
$C(s, \text{graphite})$	0	$NH_3(g)$	−16.4
$C(s, \text{diamond})$	2.900	$NO(g)$	+87.6
$CO(g)$	−137.2	$NO_2(g)$	+51.3
$CO_2(g)$	−394.4	$NaCl(s)$	−384.1





Free Energy and the Equilibrium Constant



Free Energy Determines the Direction of Spontaneous Change